

On Order-Disorder ($L2_1 \rightarrow B2'$) Phase Transition in $Ni_{2+x}Mn_{1-x}Ga$ Heusler Alloys

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PACS numbers: 64.60.Cn, S1.2

The ferromagnetic $Ni_{2+x}Mn_{1-x}Ga$ Heusler alloys are of considerable interest due to their potential applicability as magnetically driven shape memory materials¹. For the stoichiometric composition of Ni_2MnGa the melting temperature is 1382 K (Ref. 2). At cooling from the liquid phase these triple alloys usually solidify in the disordered A2 phase characterized by an arbitrary occupation of every site in the crystal lattice. In principle, the chemical ordering in solid state of Heusler alloys is possible either through an intermediate partially ordered $B2'$ phase or directly to the completely ordered body-centered cubic $L2_1$ phase³. In the $B2'$ phase Ni atoms order while Mn and Ga atoms occupy their sites in the crystal lattice randomly. However, the neutron diffraction measurements as well as the differential thermal analysis² of the Ni-Mn-Ga system presented no clear evidence for the presence of the A2 – $B2'$ phase transition, meaning presumably that these alloys solidify in the partially ordered $B2'$ phase. For the stoichiometric composition of Ni_2MnGa the $L2_1 \rightarrow B2'$ phase transition temperature is 1071 K.

At further cooling, the $Ni_{2+x}Mn_{1-x}Ga$ Heusler alloys undergo a structural phase transition from the body-centered cubic phase to the body-centered tetragonal ($c/a = 0.94$) martensitic phase, characterized by the pronounced effects of shape memory and superelasticity^{4,5,6}. For the stoichiometric Ni_2MnGa composition the martensitic transition temperature is equal to 202 K. This transition is preceded by a premartensitic transition at 260 K, which is the formation of the static displacement waves in the lattice with the wavevector $[\frac{1}{3}\frac{1}{3}0]$ (Refs. 7,8). The deviation from stoichiometry in $Ni_{2+x}Mn_{1-x}Ga$ alloys results in merging of the premartensitic and martensitic transitions, so that the tetragonal phase appears to be modulated by the static displacement waves.

While being in cubic $L2_1$ phase, Ni_2MnGa exhibits a ferromagnetic phase transition with the Curie temperature $T_C = 376$ K. The change of composition in the $Ni_{2+x}Mn_{1-x}Ga$ system results in a decrease of Curie temperature and an increase of martensitic transition temperature until they merge at $x = 0.18 - 0.20$ (Ref. 9). While the low temperature phase transitions in the $Ni_{2+x}Mn_{1-x}Ga$ system were studied in many aspects, the high temperature $L2_1 \rightarrow B2'$ phase transition needs

further investigation. In the present work we studied this transition in $Ni_{2+x}Mn_{1-x}Ga$ ($x = 0.16 - 0.20$) by means of differential scanning calorimetry (DSC) measurements.

The $Ni_{2+x}Mn_{1-x}Ga$ polycrystalline ingots were prepared by a conventional arc-melting method under argon atmosphere. The ingots were annealed at 1100 K for nine days in quartz ampoules and quenched in ice water. Samples for the measurements were cut from the middle part of the ingots. The measurements were done by a NETZSCH-404 high temperature differential scanning calorimeter in the temperature range from 750 to 1200 K.

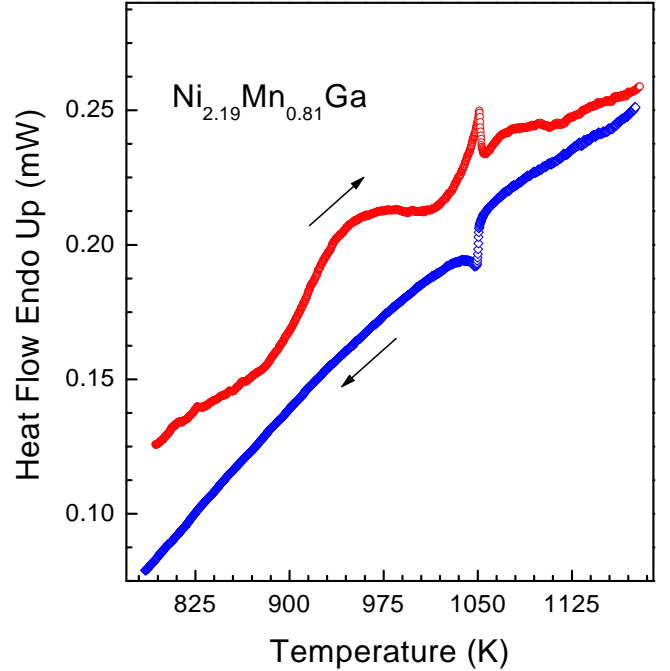


FIG. 1: DSC curves measured at heating and cooling for $Ni_{2.19}Mn_{0.81}Ga$.

The results of DSC measurements for the $Ni_{2.19}Mn_{0.81}Ga$ sample are shown in Fig. 1. The well-defined peaks on the curves obtained upon heating and cooling correspond to the $L2_1 \rightarrow B2'$ phase transition. It is evident that these anomalies are of a characteristic λ -type expected for a second order transition. No difference in the temperatures of this

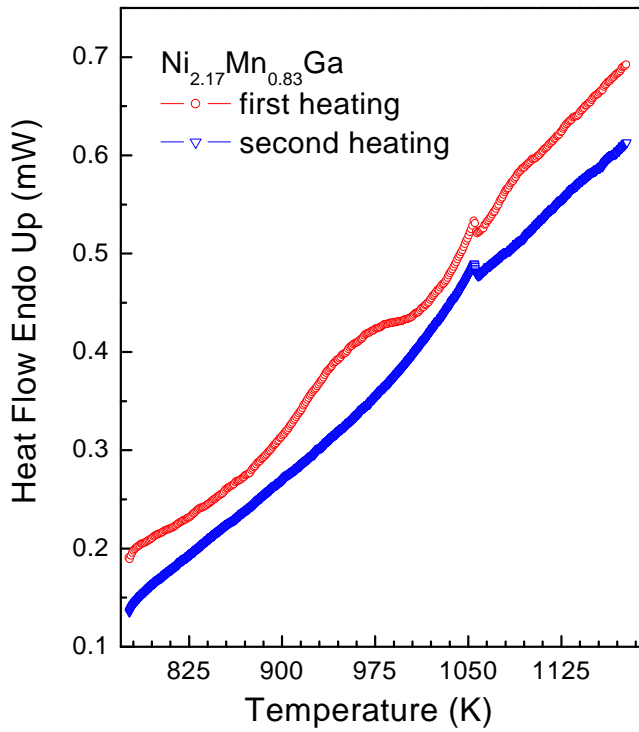


FIG. 2: Heat flow as a function of temperature during first and second heating in $\text{Ni}_{2.17}\text{Mn}_{0.83}\text{Ga}$.

phase transition in the heating and cooling cycles was detected within the experimental uncertainties. In fact, the same λ -type anomalies were seen also at $\text{B2} - \text{L2}_1$ second order phase transition in the Cu-Al-Mn system¹⁰.

An additional feature of these measurements is the appearance of a broad anomaly in a temperature range from 870 to 1030 K on the heating curve. The position of this anomaly varied randomly below the temperature of the $\text{L2}_1 \rightarrow \text{B2}'$ second order phase transition, but it was seen in every sample studied. To clarify the origin of this extra contribution, the $\text{Ni}_{2.17}\text{Mn}_{0.83}\text{Ga}$ samples were subjected to repeated heating and it was found that the broad anomalies vanish just after the first heating - cooling cycle. The results of DSC measurements obtained during first and second heating process for the $\text{Ni}_{2.17}\text{Mn}_{0.83}\text{Ga}$ sample are shown in Fig. 2. Based on these measurements it can be concluded that the additional anomalies on DSC curves appear due to the procedure of the thermal treatment. The quenching of the samples resulted in the stabilization of the partially ordered $\text{B2}'$ phase. At first heating randomly distributed Mn and Ga atoms occupy their sites in the L2_1 structure and this process is accompanied by an additional heat exchange with the calorimeter. At repeated heating these broad anomalies disappear since in the first heating and cooling cycle the samples were slowly cooled from the disordered state. Assumingly, during this procedure the Mn and Ga atoms took their sites in the L2_1 structure.

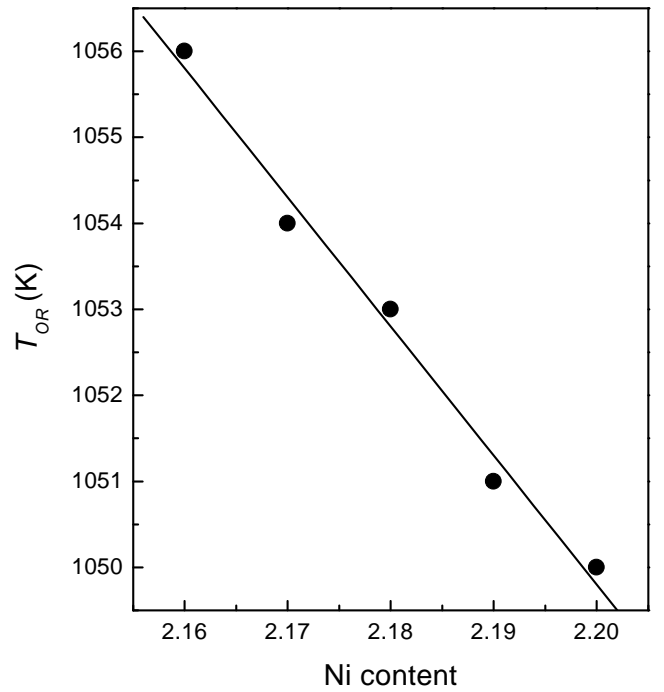


FIG. 3: The compositional dependence of the $\text{L2}_1 \rightarrow \text{B2}'$ phase transition temperature in $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ ($x = 0.16 - 0.20$).

The compositional dependence of the chemical ordering temperature T_{OR} is shown in Fig. 3. The $\text{L2}_1 \rightarrow \text{B2}'$ phase transition temperature somewhat decreases with the increase of the Ni content in $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ alloys. In fact, this tendency could be probably expected since the $\text{L2}_1 \rightarrow \text{B2}'$ phase transition temperature in Ni_3Ga is much lower than in Ni_2MnGa ($x = 0$), and the former compound could be considered formally as a limiting case of a triple alloy composition with $x = 1$ (Ref. 11).

In conclusion, it was found that the $\text{L2}_1 \rightarrow \text{B2}'$ phase transition in $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ ($x = 0.16 - 0.20$) Heusler alloys is of second order and the temperature of this transition decreases with Ni excess. Extra anomalies observed in DSC measurements during the first heating - cooling cycle below the $\text{L2}_1 \rightarrow \text{B2}'$ transition appear presumably due to the ordering of non-equilibrium $\text{B2}'$ phase obtained through quenching of the samples from high temperatures to the equilibrium L2_1 phase.

Acknowledgements

This work was partially supported by the Grant-in-Aid for Scientific Research (C) No. 11695038 from the Japan Society of the Promotion of Science and by Grant-in-Aid of the Russian Foundation for Basic Research No. 99-02-18247.

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